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(54) **ENHANCED QUALITY THIN FILM Cu(In,Ga)Se₂ FOR SEMICONDUCTOR DEVICE APPLICATIONS BY VAPOR-PHASE RECRYSTALLIZATION**

DÜNNE SCHICHT VON Cu(In,Ga)Se₂ MIT VERBESSERTER QUALITÄT DURCH DAMPFPHASENREKRISTALLISATION FÜR HALBLEITERVORRICHTUNGEN

COUCHE MINCE DE Cu(In,Ga)Se₂ DE QUALITE AMELIOREE DESTINEE A DES APPLICATIONS RELATIVES A DES DISPOSITIFS A SEMICONDUCTEURS ET PRODUITE PAR REKRISTALLISATION EN PHASE VAPEUR

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(73) Proprietor:
**Midwest Research Institute
Kansas City Missouri 64110 (US)**

(72) Inventors:
• **TUTTLE, John, R.**
Denver, CO 80204 (US)
• **CONTRERAS, Miguel, A.**
Golden, CO 80401 (US)
• **NOUFI, Rommel**
Golden, CO 80401 (US)
• **ALBIN, David, S.**
Denver, CO 80206-2945 (US)

(74) Representative:
Wagner, Karl H., Dipl.-Ing.
WAGNER & GEYER
Patentanwälte
Gewürzmühlstrasse 5
80538 München (DE)

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Description

[0001] The United States Government has rights in this invention under Contract No. DE-AC02-83CH10093 between the U.S. Department of Energy and the National Renewable Energy Laboratory, a Division of Midwest Research Institute.

Technical Field

[0002] The present invention is related generally to preparation of thin film compounds and more particularly to preparing thin film compounds of $\text{Cu}(\text{In,Ga})\text{Se}_2$ in semiconductor devices.

Background Art

[0003] Thin films of copper-indium-diselenide (CuInSe_2), copper-gallium-diselenide (CuGaSe_2), and copper-indium-gallium-diselenide ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$), all of which are sometimes generically referred to as $\text{Cu}(\text{In,Ga})\text{Se}_2$, have become the subject of considerable interest and study for semiconductor devices in recent years. They are of particular interest for photovoltaic device or solar cell absorber applications because of solar energy to electrical energy conversion efficiencies that have been shown to exceed fifteen percent (15%) in active areas and to approach fourteen percent (14%) in total areas, which is quite high for current state-of-the-art solar cell technologies. It is generally believed by persons skilled in this art that the best electronic device properties, thus the best conversion efficiencies, are obtained when the mole percent of copper is about equal to the mole percent of the indium, the gallium, or the combination of the indium and gallium in the $\text{Cu}(\text{In,Ga})\text{Se}_2$ compound or alloy. The selenium content will not generally be important to the electronic properties of the semiconductor if the growth conditions supply sufficient selenium so that it comprises about fifty atomic percent (50 at. %) of the $\text{Cu}(\text{In,Ga})\text{Se}_2$ compound to form the desired crystal lattice structures. Sulfur can also be, and sometimes is, substituted for the selenium, so the compound is sometimes referred to even more generically as $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ to comprise all of those possible combinations.

[0004] While growth of single crystal CuInSe_2 has been studied, such as in the U.S. patent No. 4,652,332, issued to *T. Ciczek*, the use of polycrystalline thin films is really more practical. Sputter depositing a ternary single phase CuInSe_2 layer, including the ability to determine the properties of the thin film, such as multilayer structures, by varying the sputter process parameters, is described by the U.S. patent No. 4,818,357, issued to *Case et al.* However, the two fabrication methods of choice are: (1) Physical vapor deposition of the constituent elements, exemplified by the process disclosed in the U.S. patent no. 5,141,564, issued to *Chen et al.*, is generally used as a research tool; and (2) The seleniza-

tion of Cu/In metal precursors by either H_2Se gas or Se vapor. The selenization technology generally exemplified by the processes described in the U.S. patent no. 4,798,660, issued to *Ermer et al.*, the U.S. patent no. 4,915,745, issued to *Pollock et al.*, and the U.S. patent no. 5,045,409, issued to *Eberspacher et al.*, is currently favored for manufacturing processes. However, thin films produced by the selenization processes usually suffer from macroscopic spacial nonuniformities that degrade performance and yield, and reproducible consistent quality from run to run is difficult to obtain and unpredictable.

[0005] An article by J. R. Tuttle et al., AIP Conference Proceedings 268, Photovoltaic Advanced Research & Development Project, Denver, CO, 1992, Pages 186-193 relates to a "novel processing and device structure in thin-film CuInSe_2 -based solar cells". This article reports the resulting film morphology and XRD spectra of representative $\text{Cu}_2\text{Se-CuInSe}_2$ mixtures in this composition range, deposited at about 500°C are shown in Figs. 1 and 2, respectively, for 7059 glass and Mo/SLS substrates.

[0006] In accordance with the present invention, a process for fabricating thin-film semiconductor devices as set forth in claim 1 is provided. Preferred embodiments of the invention are disclosed in the dependent claims.

Disclosure of Invention

[0007] Accordingly, it is a general object of this invention to provide a process that produces a better quality $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin film more consistently and more predictably than previously known processes.

[0008] It is also an object of this invention to provide a method of producing high quality $\text{Cu}(\text{In,Ga})\text{Se}_2$ homo-junctions.

[0009] Another object of the present invention is to provide a process that is capable of fabricating films of $\text{Cu}(\text{In,Ga})\text{Se}_2$ that are smooth and do not require additional processing for photovoltaic characteristics that have applications in solar and non-solar cell functions.

[0010] Still another object of this invention is to provide a process for producing high quality $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films that does not require precise control of the ratio of $\text{Cu}/(\text{In,Ga})$, thus can be scaled up easily to production of large areas and to commercial quantities.

[0011] Additional object, advantages, and novel features of the present invention shall be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by the practice of the invention or may be realized and attained by means of the instrumentalities and in combinations particularly pointed out in the appended claims.

[0012] To achieve the foregoing and other objects and in accordance with the purpose of the present invention, as embodied and broadly described herein,

the method of this invention may comprise the steps of forming a Cu-rich, phase-separated, compound mixture comprising $\text{Cu}(\text{In,Ga})\text{Se}_2\text{:Cu}_x\text{Se}$ on a substrate, and converting Cu_xSe in the mixture to $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ by exposing the Cu_xSe to (In,Ga) and Se. This conversion should be done at elevated temperatures, preferably in the range of 300-600°C.

Brief Description of Drawings

[0013] The accompanying drawings, which are incorporated in and form a part of the specifications, illustrate the preferred embodiments of the present invention, and together with the description serve to explain the principles of the invention.

Figure 1 is a cross-sectional view of a beginning stage of ternary two phase polycrystalline growth of $\text{CuInSe}_2\text{:Cu}_x\text{Se}$ on a conducting substrate in a first step of a preferred embodiment process according to the present invention;

Figure 2 is a cross-sectional illustration of an intermediate polycrystalline growth stage of the first step of the preferred embodiment process of this invention;

Figure 3 is a cross-sectional illustration of the final stage of the first step of the preferred embodiment process of this invention;

Figure 4 is a cross-sectional illustration of the beginning of the second step of the preferred embodiment process of this invention;

Figure 5 is a cross-sectional illustration of another optional resulting polycrystalline structure produced according to the present invention that is suitable for heterojunction applications;

Figure 6 is a cross-sectional illustration of one optional resulting polycrystalline structure produced according the present invention that is suitable for homojunction applications;

Figure 7 is a $\text{Cu}_2\text{Se-In}_2\text{Se}_3$ pseudobinary phase diagram that is useful in describing and understanding the processes of the present invention;

Detailed Description of the Preferred Embodiments

[0014] The processes of the present invention comprise essentially two steps for fabricating high-quality thin film $\text{Cu}(\text{In,Ga})\text{Se}_2$ - based semiconductor devices that have photovoltaic effects and are especially adaptable for solar cell applications. For purposes of simplicity, the description of the processes and claims of this invention will focus primarily on CuInSe_2 - based struc-

tures. However, it should be understood that Ga or various combinations of $\text{In}_{1-x}\text{Ga}_x$ may be substituted for the In component described in these processes and that such substitutions are considered to be equivalents for purposes of this invention. Also, as mentioned above, where several elements can be combined with or substituted for each other, such as In and Ga, in the component to which this invention is related, it is not uncommon in this art to include those combineable or interchangeable elements in a set of parentheses, such as (In,Ga). The descriptions in this specification sometimes utilizes this convenience. Finally, also for convenience, the elements are discussed with their commonly accepted chemical symbols, including copper (Cu), indium (In), germanium (Ga), selenium (Se), hydrogen (H), and molybdenum (Mo), and the like.

[0015] The first step of this invention is to deposit or grow a high conductivity, very Cu-rich, ternary, phase-separated mixture of monocrystalline or large-grain $[\text{CuInSe}_2]_8\text{:}[\text{Cu}_x\text{Se}]_{1-8}$ ($0 \leq \delta \leq 1$, $1 \leq x \leq 2$), followed by an annealing and recrystallization of the Cu_xSe phase. The second step includes keeping the temperature high enough to maintain a liquid rich Cu_xSe environment and depositing In-rich material, such as In and Se sequential or co-deposition or the binary In_ySe , in a Se gas overpressure environment to form the desired CuIn_xSe_y compound, as will be described in more detail below.

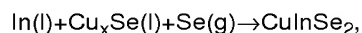
[0016] Referring now to Figure 1, the first step of a preferred embodiment process according to this invention may start by beginning the deposition of the Cu-rich thin film of $\text{CuInSe}_2\text{:Cu}_x\text{Se}$ on a substrate 12. The substrate 12 may be, for example, soda-lime silica glass or amorphous 7059 glass. The deposition can be on the bare glass substrate 12, but it may be preferred to include a smooth metallic surface 14, such as a 2000Å layer of molybdenum (Mo).

[0017] As illustrated in the phase diagram of Figure 7, when the Cu, In, and Se components are in the Cu-rich range, i.e., where the mole % of In and Se is in the range between 0-50%, and at temperatures under about 790°C, the CuInSe_2 and Cu_xSe phases are separated. Therefore, as Cu, In, and Se are deposited on the Mo-coated substrate 12 in Figure 1 in a very Cu-rich mixture, preferably comprising about 40-50 at. % Cu, at a substrate temperature greater than 500°C (preferably about 500-550°C), the CuInSe_2 crystalline structures 16 grow separate from the Cu_xSe crystalline structures 18, i.e., they are phase-separated. Also, the melting point of the Cu_xSe is slightly lower than the melting point of CuInSe_2 . Therefore, it is preferable to maintain the substrate in the above-described temperature range, where the CuInSe_2 is a solid, and the Cu_xSe is substantially in a liquid flux. Then, as the deposition process continues, as illustrated in Figure 2, the CuInSe_2 phase crystals 16 tend to grow together on the Mo layer 14, displacing the more liquid Cu_xSe phase 18 outwardly. The end result of the deposition stage of the first step illustrated in Figure 3, is a large-grain CuInSe_2 phase 16 adhered to the

Mo coating 14 with an overlayer of the Cu_xSe material 18 on its outer surface. If the CuInSe_2 and Cu_xSe compounds are deposited sequentially or at lower temperatures, this structure is then preferably annealed in a Se atmosphere, such as Se or H_2Se vapor, at a temperature of about 500-550°C. In this annealing stage, any solid Cu_xSe 18 is converted to liquid Cu_xSe , and a growth/recrystallization is believed to occur in a liquid flux environment of the Cu_xSe binary phase. This growth/recrystallization process encourages monocrystalline (112), large-grain growth (2-10 μm), which is a superior morphology for device quality electronic properties. The resulting structure of Figure 3 is referred to as the large-grain precursor 20, which forms the structural platform for a thin film electronic device fabricated according to the second step of this invention described below.

[0018] In the second step of a preferred embodiment of this invention, the excess Cu_xSe 18 in the large-grain precursor structure 20 is converted to a CuIn_ySe_z material by exposure to an activity of In and Se at elevated temperatures for a period of time, as illustrated in Figure 4. The In and Se exposure can be in the form of In vapor 22 and Se vapor 24, as illustrated in Figure 4, or it can be In_ySe solid, such as the In_2Se_3 illustrated in Figure 7, with no Cu content. With the substrate 12 and large-grain precursor structure 20 maintained in the range of about 300-600°C, the Cu_xSe overlayer 18 absorbs and combines with the In 22 to form the desired CuIn_ySe_z material. Alternatively, this conversion of Cu_xSe to a CuIn_ySe_z material can be accomplished by sequential deposition of In and Se on the precursor structure 20. The characteristic of the CuIn_ySe_z material can be controlled by the temperature maintained during this second step of the process, as described below.

[0019] A high temperature treatment option of the second step of the process, such as in the range of about 500-600°C, is illustrated in Figure 4, and the resulting nearly homogenous film structure 40 is shown in Figure 5. Essentially, at temperatures in the range of about 500-600°C, preferably at about 550°C, the Cu_xSe overlayer 18 forms a liquid flux, while the CuInSe_2 underlayer 16 remains substantially solid. The In vapor 22 condenses to liquid phase 26 at the surface of the Cu_xSe overlayer 18. The liquid In 26 and Se gas 24 contacts the overlayer 18, where it combines at the surface with the excess Cu_xSe to form additional CuInSe_2 , as shown at 28. This new CuInSe_2 remains in solution while it diffuses, as shown at 30, through the Cu_xSe overlayer 18 to the liquid-solid interface 32, where it nucleates and "epitaxial" builds on the original CuInSe_2 crystalline structures 16, as shown at 34. The nucleation can be described as:



where (l) indicates liquid and (g) indicates gas. While it is not known for certain, it is believed that the lesser

density of the CuInSe_2 in the Cu_xSe assists in transferring the CuInSe_2 to the liquid-solid interface 38. In any event, this process results in a substantially continuous morphology homogenous film growth of the CuInSe_2 crystalline structures 16. When the liquid phase Cu_xSe in the overlayer 18 is substantially consumed, the resulting film structure 40 may be near stoichiometric with planar surfaces, as shown in Figure 5. This recrystallization process is self-limiting in that, if the Se to In ratio is lowered, the process rejects In in the form of In_ySe when the surface converts from Cu-rich to Cu-poor. It may be slightly Cu-rich or slightly Cu-poor, depending on the extent of Cu_xSe recrystallization in this second step. However, the self-limiting nature of the reaction makes it unnecessary to regulate the In precisely, thus, the process is conducive to commercial processing. The nature of the surface 42 of structure 40 is known to be Cu-poor with a composition equivalent to the CuIn_3Se_5 phase and is nearly planar and smooth. Proper engineering of this surface can lead to a layer of CuIn_3Se_5 of sufficient thickness to produce a shallow homojunction, which in turn may not require the thin CdS buffer layer to make an operational solar cell. This film structure 40, which is essentially p-type CuInSe_2 , can be used on one side of a heterojunction device, as will be obvious to persons having ordinary skill in this art, by overlaying it with a different material, such as a CdS and ZnO window layer (not shown).

[0020] A lower temperature treatment option in the second step of the process of this invention, such as in the range of about 300-400°C, can produce a homojunction thin-film device 50, as shown in Figure 6, that does not require a different material overlay, such as a CdS and ZnO window layer, to have photovoltaic characteristics. In this optional lower temperature range treatment, the conversion of excess Cu_xSe to a form of CuIn_ySe_z is inhibited from approaching the stoichiometric ratio by the limited mobility of Cu at the lower temperatures, thus resulting in an overlayer 52 of very Cu-poor morphology, such as $\text{Cu}_2\text{In}_4\text{Se}_7$ in the γ'' range or CuIn_3Se_5 in the γ''' range of the phase diagram in Figure 7. Such Cu-poor structures in the overlayer 52 are n-type materials, in contrast to the p-type Cu-rich CuInSe_2 crystalline structures 16 underlying the n-type layer 52. Therefore, the interface between the underlayer 16 and overlayer 52 forms a homojunction, and the film structure 50 can function as a photovoltaic device.

[0021] There are numerous practical options and variations for fabricating thin film devices according to this invention. Substitution of Ga or a combination of In and Ga for the In described above, as well as the option of using Se vapor, H_2Se vapor, or In_ySe_z solids have already been mentioned. In addition, there are many options for deposition. For example, the deposition can be accomplished by sputtering of the two compounds CuInSe_2 and Cu_xSe in the first step either concurrently or sequentially, followed by or concurrently with Se treatment, or by co-evaporation of the constituent ele-

ments in an overpressure of Se, or by any combination of methods that will produce a phase-separated mixture of these compounds.

[0022] In other variations, the initial deposition does not have to include both of the compounds $\text{Cu}(\text{In,Ga})\text{Se}_2$ and Cu_xSe for the large-grain precursor mixture. It can start instead with an initial deposition of a binary Cu_{2-3}Se precursor as an extreme case of the $\text{Cu}(\text{In,Ga})\text{Se}_2:\text{Cu}_{2-3}\text{Se}$ large-grain precursor mixture, in which case the In and/or Ga would have to be added in a manner and at a temperature in which phase-separated $\text{Cu}(\text{In,Ga})\text{Se}_2:\text{Cu}_x\text{Se}$ would be produced on the substrate, such as by the addition of a small amount of In_2Se_3 . Of course, the initial deposition of Cu_{2-3}Se should be at a lower temperature to get the desired large-grain formation. The formation of the precursor can be dissected further by the conversion of an elemental mixture of Cu, (In,Ga), and Se to the compound mixture by exposure to Se vapor at elevated temperatures, or by the conversion of Cu and (In,Ga) to $\text{Cu}(\text{In,Ga})\text{Se}_2$ by exposure to H_2Se . At the other extreme, an initial deposition of In_2Se_3 could be made in conjunction with a larger amount of Cu_2Se . The goal, regardless of which combination or sequence of materials deposition is used, is to achieve the Cu-rich, phase separated growth of the $\text{Cu}(\text{In,Ga})\text{Se}_2:\text{Cu}_x\text{Se}$ mixture in the first step of the process, so that the second step can proceed according to that portion of this invention. Also, additional Cu as well as, or instead of, the additional In can be incorporated in the second step.

Examples

[0023] Absorbers according to this invention were fabricated by a combination of physical vapor deposition and $\text{H}_2\text{Se}/\text{Se}$ vapor selenization on 5-cm x 5-cm (2-in x 2-in) Mo-coated soda-lime silica (SLS) and bare 7059 glass at substrate temperatures in excess of 550°C. At times, an intentional one-dimensional compositional gradient was introduced across the 5-cm substrate to facilitate the study of novel device structures and the relationship between device parameters and film composition. Absorbers included CuInSe_2 , $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0.0 \leq x \leq 0.25$), and $\text{CuGaSe}_2/\text{CuInSe}_2$ layered structures. Surface and bulk material characterization were accomplished by Auger electron spectroscopy (AES), X-ray and ultraviolet photoemission spectroscopy (XPS, UPS), X-ray and transmission-electron diffraction (XRD, TED), photoluminescence (PL), and analytical scanning electron microscopy (ASEM). Device characterization was accomplished by dark and light I-V and spectral response at temperatures down to 50K, capacitance-voltage, and deep-level transient spectroscopy (DLTS).

[0024] We were successful in producing device quality CuInSe_2 based thin films on bare glass and Mo-coated SLS with columnar structures and a lateral grain size of 2.0-10.0 μm . XRD studies suggest monocrystalline behavior on bare substrates, and (112) high pre-

ferred orientation on Mo-coated substrates. XRD and TED confirmed the presence of a CuPt-type ordering of Cu and In planes within the bulk of the film. We attribute the creation of this phase to the high substrate temperatures and liquid-phase assisted growth processes present.

[0025] In film structures with an overall Cu-rich composition, the Cu_2Se binary phase was identified at the surface by XPS and within the bulk by EDS of thinned samples prepared in cross section for TED. In film structures with an overall Cu-poor composition, the $\text{CuIn}_2\text{Se}_{3.5}\text{Y}'$ ordered-vacancy compound (OVC) phase was observed in the bulk by XRD and TED, while the $\text{CuIn}_3\text{Se}_5\text{Y}''$ OVC is exclusively observed at the surface. Electrical characterization of the Y' and Y'' phases [3] indicated enhanced transport properties and n-type behavior. Electrical activity within the grain and at grain-boundaries in these films were not discernibly different.

[0026] Process-dependent device structures included both sharp heterojunctions and deep homo-junctions, with an observed space-charge width of up to 2.5 μm . Heterojunction cells were completed with either a thick CdS window layer deposited by physical vapor deposition, or with a chemical-bath deposition (CBD) CdS (700Å)/ZnO (0.5 μm) layered window. Photovoltaic (PV) devices with conversion efficiencies in excess of 12% and most recently over 13.7% have been demonstrated. Films that were fabricated with an intentional compositional gradient exhibited an open-circuit voltage (V_{oc}) vs. composition dependence, while the short-circuit current (J_{sc}) remained constant over a wide compositional range. A very promising structure involved the growth of CuInGaSe_2 on CuGaSe_2 . Open circuit voltages ranging from 550 to 630 mV and J_{sc} 's ranging from 37 to 30 mA/cm^2 have been observed, respectively. Thus result suggests total area device efficiencies greater than 15% are possible. The voltage parameter was significant in light of the analysis (AES depth profiling and spectral response), which measured a surface and content less than that usually required to obtain the device parameters quoted. It is suggested that a back-surface field from the CuGaSe_2 was contributing to the voltage enhancement of the CuInSe_2 absorber. We anticipate significant improvements in the near future as the processes are optimized.

[0027] We have been successful in producing enhanced-grain device-quality $\text{Cu}(\text{In,Ga})\text{Se}_2$ by a simple two-stage process. The first stage of the process involved the growth of an enhanced-grain CuInSe_2 aggregate mixture. At high substrate temperatures, the growth of the CuInSe_2 occurred in a liquid rich environment, which accounted for the increase in average grain size of the film mixture. When the vapor flux became In-rich, the CuInSe_2 formed at the surface remained in solution while it diffused to the liquid-solid interface, where it condensed, nucleated and "epitaxial" built on the original CuInSe_2 surface. When the liquid phase was consumed, the process was terminated in some

samples and in others by In diffusion into the bulk or by the growth of very Cu-poor phases near the surface. The latter step determined the homo-or hetero junction nature of the device. This generalized procedure may be applied to scalable manufacturing processes, like sputtering and selenization, in a very reproducible manner.

[0028] The foregoing description is considered as illustrative only of the principles of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and process shown as described above. Accordingly, all suitable modifications and equivalents may be resorted to falling within the scope of the invention as defined by the claims which follow.

Claims

1. A process for fabricating thin film semiconductor devices, comprising the steps of:
 - forming a Cu-rich, phase separated, compound mixture (20) comprising $\text{Cu}(\text{In,Ga})\text{Se}_2\text{:Cu}_x\text{Se}$ (16;18) on a substrate (12); and
 - converting Cu_xSe (18) in the mixture (20) to $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ by exposing said Cu_xSe (18) to (In,Ga) and Se.
2. The process of claim 1, including the step of forming said mixture (20) in a temperature range of about 500-600°C.
3. The process of claim 1, including the step of converting said Cu_xSe (18) to $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ in a temperature range of about 500-600°C.
4. The process of claim 3, including the step of converting said Cu_xSe (18) to $\text{Cu}(\text{In,Ga})\text{Se}_2$.
5. The process of claim 1, including the step of converting said Cu_xSe (18) to $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ in a temperature range of about 300-400°C.
6. The process of claim 5, including the step of converting said Cu_xSe (18) to $\text{Cu}_2(\text{In,Ga})_4\text{Se}_7$.
7. The process of claim 5, including the step of converting said Cu_xSe (18) to $\text{Cu}(\text{In,Ga})_3\text{Se}_5$.
8. The process of claim 1, wherein $1 \leq x \leq 2$.
9. The process of claim 1, wherein the ratio of $\text{Cu}(\text{In,Ga})_2\text{:Cu}_x\text{Se}$ (16;18) is about 1:2.
10. The process of claim 1, wherein Cu comprises about 40-50 atomic percent of said mixture (20).
11. The process of claim 1, including the step of exposing said Cu_xSe (18) to In_ySe_z .
12. The process of claim 11, including the step of exposing said Cu_xSe (18) to In_2Se_3 .
13. The process of claim 1, including the step of exposing said Cu_xSe (18) to In vapor (22) and Se vapor (24).
14. The process of claim 1, including the step of forming said mixture (20) by depositing said $\text{Cu}(\text{In,Ga})\text{Se}_2$ and said Cu_xSe on said substrate.
15. The process of claim 14, including the step of forming said mixture (20) by depositing $\text{Cu}(\text{In,Ga})\text{Se}_2$ and Cu_xSe on said substrate simultaneously.
16. The process of claim 14, including the step of forming said mixture (20) by depositing $\text{Cu}(\text{In,Ga})\text{Se}_2$ and Cu_xSe sequentially.
17. The process of claim 1, including the step of forming said mixture (20) by depositing Cu_xSe and In_ySe_z .
18. The process of claim 17, including the step of depositing said Cu_xSe and said In_ySe_z sequentially.
19. The process of claim 17, including the step of depositing said Cu_xSe and said In_ySe_z simultaneously.
20. The process of claim 7, where said Cu_xSe is further defined by $1 \leq x \leq 2$, and where said In_ySe_z is further defined by $y=2$ and $z=3$.
21. The process of claim 17, including the step of depositing said Cu_xSe by first depositing Cu and then exposing said Cu to Se.
22. The process of claim 14, including the step of depositing said $\text{Cu}(\text{In,Ga})\text{Se}_2$ by depositing an elemental mixture of Cu and (In,Ga) and exposing said mixture to Se.
23. The process of claim 14, including the step of depositing said mixture (20) by sputtering.
24. The process of claim 14, including the step of depositing said mixture (20) by physical co-evaporation.
25. The process of claim 1, wherein said substrate (12) comprises glass.
26. The process of claim 25, wherein said substrate (12) comprises a Mo coating (14) on said glass.

Patentansprüche

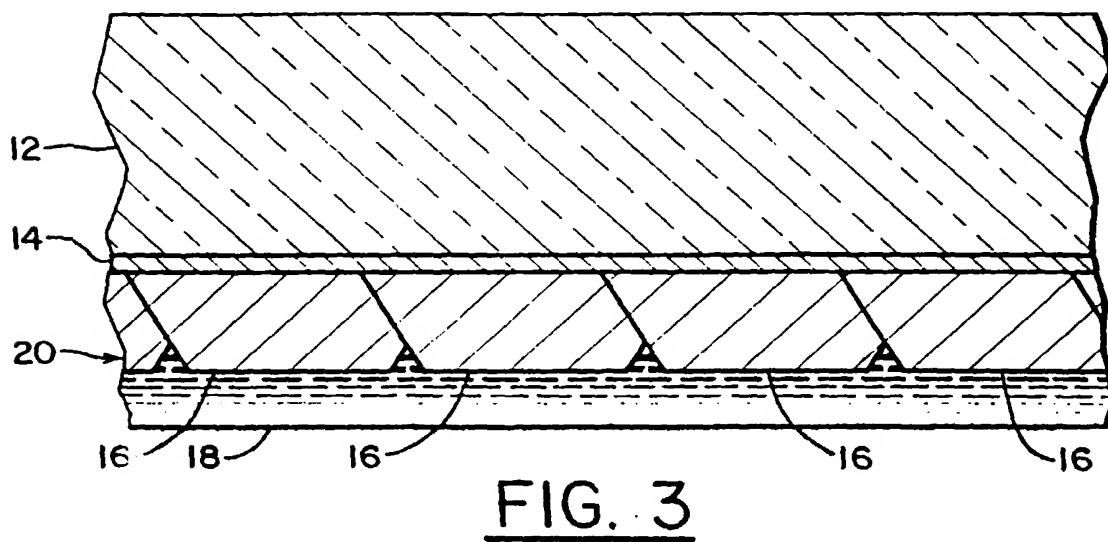
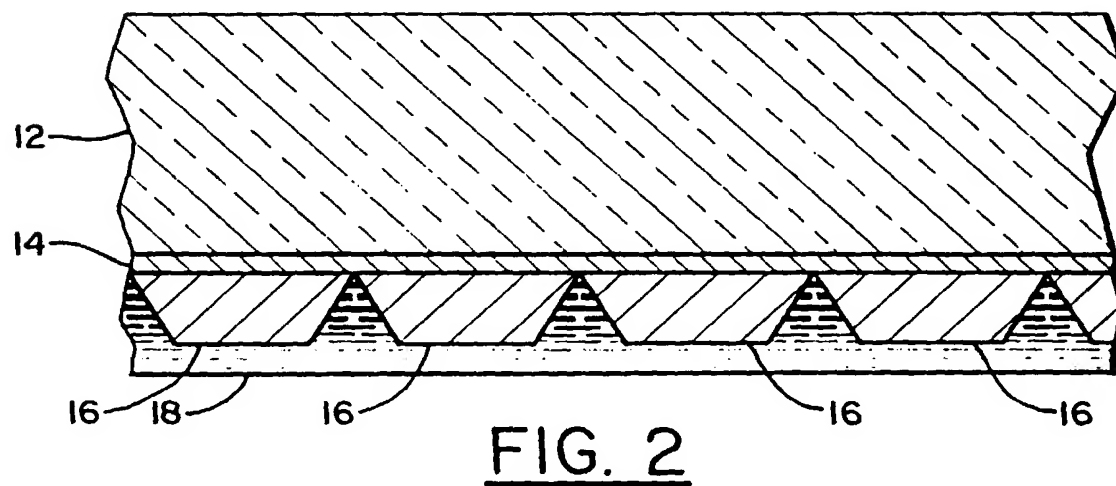
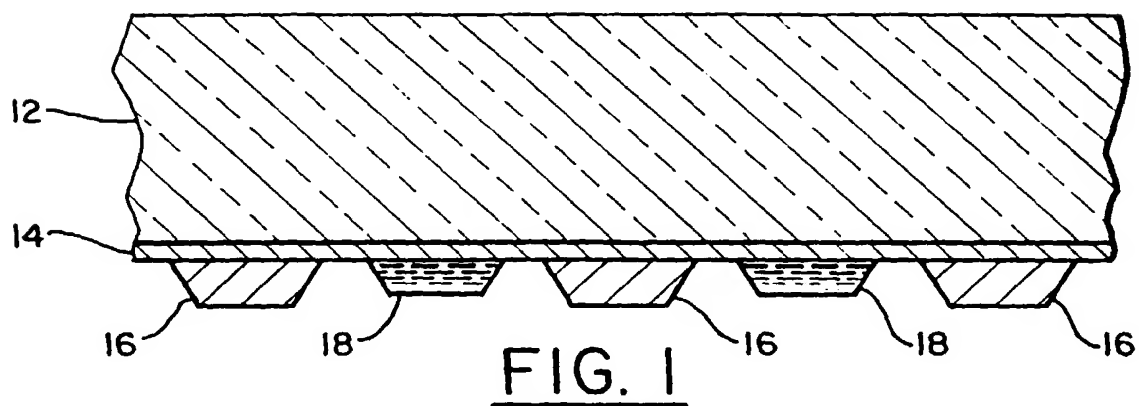
1. Verfahren zur Herstellung von Dünnschicht-Halbleitervorrichtungen, das folgende Schritte aufweist:

Ausbildung einer Cu-reichen, phasengeordneten Verbundmischung (20), die $\text{Cu}(\text{In,Ga})\text{Se}_2\text{:Cu}_x\text{Se}$ (16; 18) auf einem Substrat (12); und

Umwandlung des Cu_xSe (18) in der Mischung (20) zu $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ durch Aussetzen des Cu_xSe (18) gegen (In,Ga) und Se.
2. Verfahren nach Anspruch 1, das den Schritt der Ausbildung der Mischung (20) in einem Temperaturbereich von ungefähr 500-600°C aufweist.
3. Verfahren nach Anspruch 1, das den Schritt der Umwandlung des Cu_xSe (18) zu $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ in einem Temperaturbereich von ungefähr 500-600°C aufweist.
4. Verfahren nach Anspruch 3, das den Schritt der Umwandlung des Cu_xSe (18) in $\text{Cu}(\text{In,Ga})\text{Se}_2$ aufweist.
5. Verfahren nach Anspruch 1, das den Schritt der Umwandlung des Cu_xSe (18) in $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ in einem Temperaturbereich von ungefähr 300-400°C aufweist.
6. Verfahren nach Anspruch 5, das den Schritt der Umwandlung des Cu_xSe (18) in $\text{Cu}_2(\text{In,Ga})_4\text{Se}_7$ aufweist.
7. Verfahren nach Anspruch 5, das den Schritt der Umwandlung des Cu_xSe (18) in $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ aufweist.
8. Verfahren nach Anspruch 1, wobei $1 \leq x \leq 2$ ist.
9. Verfahren nach Anspruch 1, wobei das Verhältnis von $\text{Cu}(\text{In,Ga})_2\text{:Cu}_x\text{Se}$ (16; 18) ungefähr 1:2 ist.
10. Verfahren nach Anspruch 1, wobei Cu ungefähr 40-50 Atomprozent der Mischung (20) stellt bzw. aufweist.
11. Verfahren nach Anspruch 1, das den Schritt des Aussetzens des Cu_xSe (18) gegen In_ySe_z aufweist.
12. Verfahren nach Anspruch 11, das den Schritt des Aussetzens des Cu_xSe (18) gegen In_2Se_3 aufweist.
13. Verfahren nach Anspruch 1, das den Schritt des Aussetzens des Cu_xSe (18) gegen In-Dampf (22) und gegen Se-Dampf (24) aufweist.
14. Verfahren nach Anspruch 1, das den Schritt der Ausbildung der Mischung (20) durch Abscheiden des $\text{Cu}(\text{In,Ga})\text{Se}_2$ und des Cu_xSe auf dem Substrat aufweist.
15. Verfahren nach Anspruch 14, das den Schritt der Ausbildung der Mischung (20) durch Abscheiden von $\text{Cu}(\text{In,Ga})\text{Se}_2$ und Cu_xSe auf dem Substrat simultan aufweist.
16. Verfahren nach Anspruch 14, das den Schritt der Ausbildung der Mischung (20) durch Abscheiden von $\text{Cu}(\text{In,Ga})\text{Se}_2$ und Cu_xSe aufeinanderfolgend aufweist.
17. Verfahren nach Anspruch 1, das den Schritt der Ausbildung der Mischung (20) durch Abscheiden von Cu_xSe und In_ySe_z aufweist.
18. Verfahren nach Anspruch 17, das den Schritt des Abscheidens des Cu_xSe und des In_ySe_z aufeinanderfolgend aufweist.
19. Verfahren nach Anspruch 17, das den Schritt des Abscheidens des Cu_xSe und des In_ySe_z simultan aufweist.
20. Verfahren nach Anspruch 7, wobei das Cu_xSe ferner definiert ist durch $1 \leq x \leq 2$, und wobei das In_ySe_z ferner definiert ist durch $y=2$ und $z=3$.
21. Verfahren nach Anspruch 17, das den Schritt des Abscheidens des Cu_xSe durch eine erste Abscheidung von Cu und dann das Aussetzen des Cu gegen Se aufweist.
22. Verfahren nach Anspruch 14, das den Schritt des Abscheidens von $\text{Cu}(\text{In,Ga})\text{Se}_2$ durch Abscheidung einer Elementmischung von Cu und (In,Ga) und das Aussetzen der Mischung gegen Se aufweist.
23. Verfahren nach Anspruch 14, das den Schritt des Abscheidens der Mischung (20) durch Sputtern aufweist.
24. Verfahren nach Anspruch 14, das den Schritt des Abscheidens der Mischung (20) durch physikalische Koverdampfung aufweist.
25. Verfahren nach Anspruch 1, wobei das Substrat (12) Glas aufweist.
26. Verfahren nach Anspruch 25, wobei das Substrat (12) eine Mo-Beschichtung (14) auf dem Glas aufweist.

Revendications

1. Procédé de fabrication de dispositifs semiconducteurs en couches minces comprenant les étapes suivantes :
 former un mélange complexe, séparé en phase, riche en Cu (20) comprenant $\text{Cu}(\text{In,Ga})\text{Se}_2\text{:Cu}_x\text{Se}$ (16 ; 18) sur un substrat (12) ; et
 convertir Cu_xSe (18) dans le mélange (20) en $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ en exposant le Cu_xSe (18) à (In,Ga) et à Se.
2. Procédé selon la revendication 1, comprenant l'étape consistant à former le mélange (20) dans une plage de température d'environ 500 à 600°C.
3. Procédé selon la revendication 1, comprenant l'étape consistant à convertir Cu_xSe (18) en $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ dans une plage de température d'environ 500 à 600°C.
4. Procédé selon la revendication 3, comprenant l'étape consistant à convertir Cu_xSe (18) en $\text{Cu}(\text{In,Ga})\text{Se}_2$.
5. Procédé selon la revendication 1, comprenant l'étape consistant à convertir Cu_xSe (18) en $\text{Cu}_w(\text{In,Ga})_y\text{Se}_z$ dans une plage de température d'environ 300 à 400°C.
6. Procédé selon la revendication 5, comprenant l'étape consistant à convertir Cu_xSe (18) en $\text{Cu}_2(\text{In,Ga})_4\text{Se}_7$.
7. Procédé selon la revendication 5, comprenant l'étape consistant à convertir Cu_xSe (18) en $\text{Cu}(\text{In,Ga})_3\text{Se}_5$.
8. Procédé selon la revendication 1, dans lequel $1 \leq x \leq 2$.
9. Procédé selon la revendication 1, dans lequel le rapport de $\text{Cu}(\text{In,Ga})\text{Se}_2\text{:Cu}_x\text{Se}$ (16 ; 18) est d'environ 1/2.
10. Procédé selon la revendication 1, dans lequel Cu constitue environ 40 à 50 % en atomes du mélange (20).
11. Procédé selon la revendication 1, comprenant l'étape composant à exposer le Cu_xSe (18) à In_ySe_z .
12. Procédé selon la revendication 11, comprenant l'étape composant à exposer Cu_xSe (18) à In_2Se_3 .
13. Procédé selon la revendication 1, comprenant l'étape consistant à exposer Cu_xSe (18) à une vapeur d'In (22) et à une vapeur de Se (24).
14. Procédé selon la revendication 1, comprenant l'étape consistant à former le mélange (20) en déposant $\text{Cu}(\text{In,Ga})\text{Se}_2$ et Cu_xSe sur ledit substrat.
15. Procédé selon la revendication 14, comprenant l'étape consistant à former le mélange (20) en déposant $\text{Cu}(\text{In,Ga})\text{Se}_2$ et Cu_xSe simultanément sur le substrat.
16. Procédé selon la revendication 14, comprenant l'étape consistant à former le mélange (20) en déposant $\text{Cu}(\text{In,Ga})\text{Se}_2$ et Cu_xSe séquentiellement.
17. Procédé selon la revendication 1, comprenant l'étape consistant à former le mélange (20) en déposant Cu_xSe et In_ySe_z .
18. Procédé selon la revendication 17, comprenant l'étape consistant à déposer Cu_xSe et In_ySe_z séquentiellement.
19. Procédé selon la revendication 17, comprenant l'étape consistant à déposer Cu_xSe et In_ySe_z simultanément.
20. Procédé selon la revendication 7, dans lequel Cu_xSe est en outre défini par $1 \leq x \leq 2$, et In_ySe_z est en outre défini par $y=2$ et $z=3$.
21. Procédé selon la revendication 17, comprenant l'étape consistant à déposer le Cu_xSe en déposant d'abord Cu et en exposant ensuite Cu à Se.
22. Procédé selon la revendication 14, comprenant l'étape consistant à déposer le $\text{Cu}(\text{In,Ga})\text{Se}_2$ en déposant un mélange élémentaire de Cu et (In,Ga) et en exposant le mélange à Se.
23. Procédé selon la revendication 14, comprenant l'étape consistant à déposer le mélange (20) par pulvérisation.
24. Procédé selon la revendication 14, comprenant l'étape consistant à déposer le mélange (20) par co-évaporation physique.
25. Procédé selon la revendication 1, dans lequel le substrat (12) comprend du verre.
26. Procédé selon la revendication 25, dans lequel le substrat (12) comprend un revêtement de Mo (14) sur le verre.



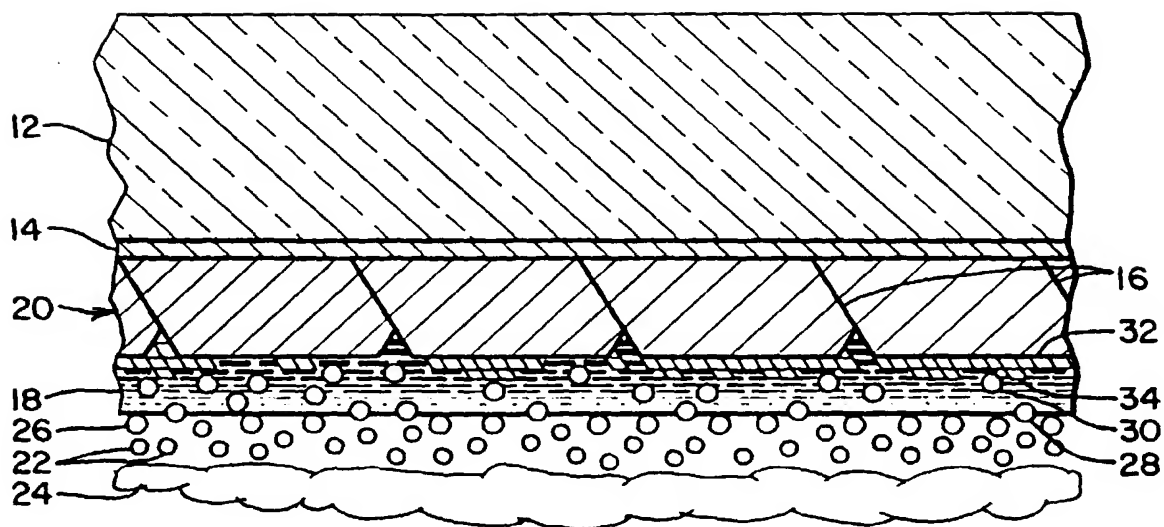


FIG. 4

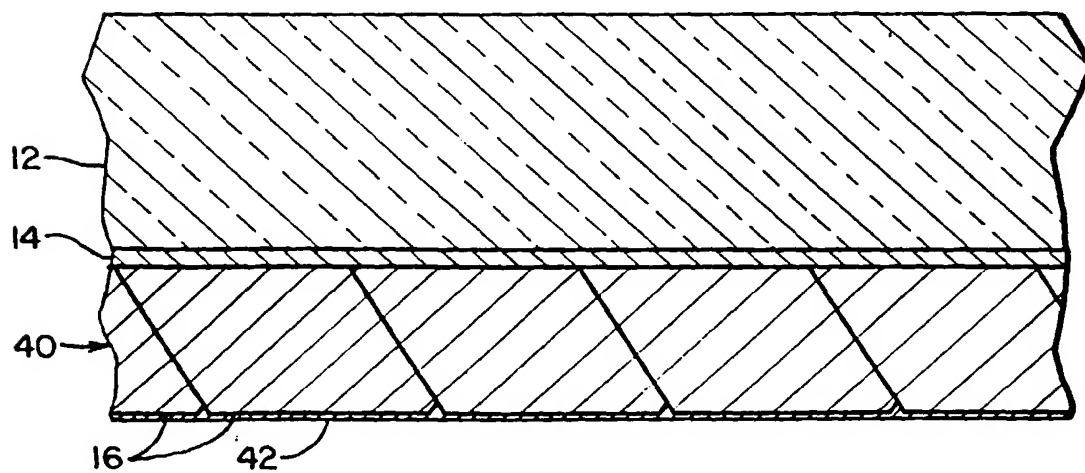


FIG. 5

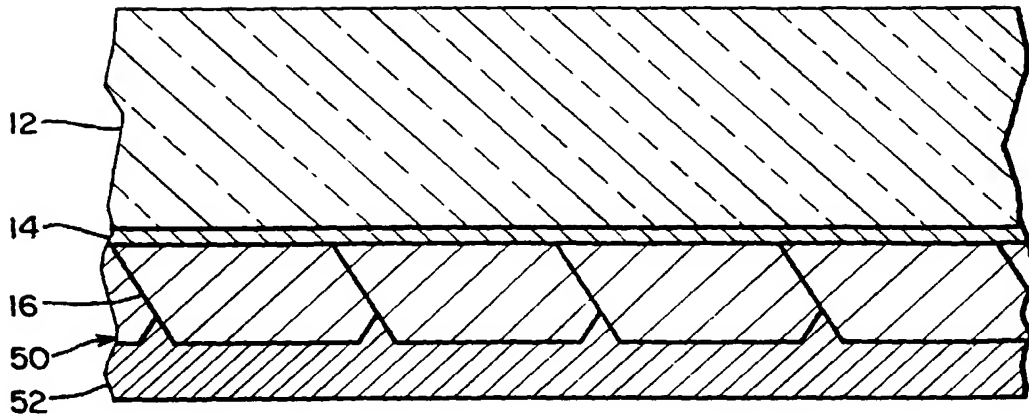


FIG 6

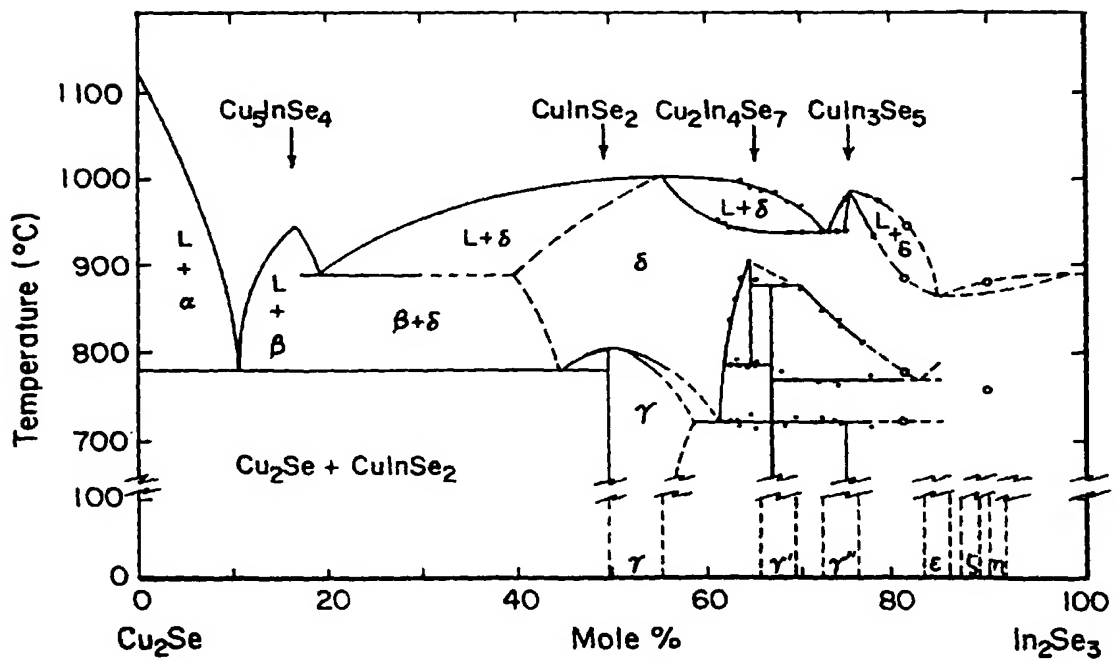


FIG. 7